RAW MATERIALS

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ALKALI KAOLINS OF UKRAINE — COMPLEX RAW MATERIALS FOR THE CERAMICS INDUSTRY

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The characteristics of the mineral and chemical compositions of the deposits of alkali kaolins of Ukraine are presented, and the advantages of enrichment and use of complex raw materials for the production of porcelain articles are shown.

Key words: complex ceramic raw material, alkali kaolins.

Conventionally, plastic (kaolins and clays) and nonplastic (stony) materials are used in the production of domestic ceramic. They are added to regulate the technological properties of the ceramic mix: to lower the sintering temperature of the articles, decrease the deformation in the process of their heat treatment, increase the heat resistance, and many others. Among them the potassium and sodium minerals are of greatest importance — feldspars (orthoclase, albite, anortite), nepheline, and wollastonite. The conventional source of feldspars for the ceramics industry is pegmatite. However, pegmatite raw material is in short supply, so that at present diverse complex raw materials characterized by a high content of potassium feldspars, to which alkali kaolins belong, are widely used in the industry. It should be noted that the high potassium content (K_2O content > 2%),[2] due to the presence of fine-grain microcline and orthoclase crystals in them, as well as potassium micas make them suitable for use as substitutes for potassium-feldspar raw material in the production of ceramics.

Kaolin deposits located at the site of their formation are represented by the final product of erosion of feldspar rocks or hydrothermal formation transformation of the enclosing rock. The inherited structure of the parent rock is characteristic for many primary kaolins formed along well crystallized rocks [1]. In the opinion of specialists, kaolins formed along granites, metamorphic gneisses, and migmatites are most widely seen and are of greatest significance; examples are the kaolins of the Prosyanovskoe (Dnepropetrovsk Oblast'), Beregovskoe (Zakarpatskaya Oblast'), and Glukhovetskoe (Vinnitsa Oblast') deposits.

At the present time the largest production volumes of Ukrainian kaolins are found in Dnepropetrovsk and Zaporozhe Oblast's. However, with respect to the prospects of explored deposits the leader is Vinnitsa oblast, where the reserves of kaolin raw material are about 558×10^6 tons [2].

The most productive kaolin regions of the northwesters subprovinces are Maidano-Dubrovkii (Zhitomir Oblast') and Turbovsko-Glukhovetskii (northern Vinnitsa Oblast').

Dubrovskaya group of alkali kaolins is located in Zhitomir Oblast'. In this group the most desirable reserves are alkali kaolins formed along the Korostyshev pegmatoids and Zhitomir medium-grain granites. The mineral composition of the Dubrovskoe kaolins is as follows (%): kaolinite — 24; microcline — 21; quartz — 48. The sand component of the kaolinized rock is 70 – 80% microcline and quartz with an admixture (5 – 10%) coarse-flake muscovite. The microcline content in the kaolin raw product is 18 – 25% and the quartz content is 30 – 40%.

The largest deposit of primary kaolin in the Dubrovskaya group is the Velikogadomskoe deposit located at the border between Vinnitsa and Zhitomir Oblast's. The kaolin content in rock is about 60%; its mineral composition is (%): kaolinite — 50; potassium feldspar — 12.5; quartz — 25. The distinguishing feature of kaolins of this deposit is the extreme whiteness of the kaolin concentrate, reaching 90%. It should be note that the alkali kaolins of this deposit are characterized by low mechanical strength (0.3 – 0.6 MPa), and

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[2] Here and below — content by weight.

TABLE 1. Chemical Composition of Natural and Enriched Alkali Kaolins in Ukraine

Deposit	Content by weight, %								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	others
Dubrovskoe (r)	67 – 75	18 – 30	> 0.5	0.4 – 0.7	0.1	0.25	4.08	0.70	3.54
Dubrovskoe (e)	48.00	36.15	0.90	0.17	0.45	0.73	1.70	0.30	11.80
Ekaterinskoe (r)	71.73	17.27	0.47	0.30	0.36	0.19	6.11	0.29	3.28
Prosyanovskoe (r)	71.43	19.14	0.35	0.29	0.25	0.06	2.98	0.06	5.25
Prosyanovskoe (e)	46.96	38.19	0.44	0.30	0.26	0.05	4.50	Traces	13.51
Belaya Balka (r) (Bogoroditskoe)	62.05	20.25	0.65	0.76	0.78	0.27	3.03		8.50
Belaya Balka (e) (Bogoroditskoe)	47.0	37.55	0.89	1.74	1.80	0.34	1.35		12.88
Velikogadomskoe (r)	66.09	20.96	0.26	0.34	0.10	0.10	2.26	0.08	3.46
Velikogadomskoe (e)	48.69	35.96	0.44	0.56	0.05	0.09	1.47	0.05	12.05

Notations: r) kaolin-raw; e) enriched kaolin.

for this reason they are used in the production of fine ceramic and electrotechnical ceramic only at additives (in amounts 20 – 50%) to stronger kaolins, specifically, Prosyanovskoe kaolin.

One of the best known groups of primary alkali feldspar-containing kaolins from the Pridpneprovskaya subprovince is the Prosyanovskoe group (Dnepropetrovsk Oblast'). The kaolin content in rock is 45 – 72%. The mineral composition of Prosyanovskoe kaolin is as follows (5): kaolinite — 35; potassium feldspar — 25; quartz — 31. The sand component is 35 – 50% microcline. The whiteness of the kaolin is greater than 88%. The reserves of the deposits of this group are about 30×10^6 tons [3].

Covering the territories of the Donetsk, Zaporozhe, and Kherson Oblast's, the Priazovskaya subprovince is characterized by high alkalinity of the primary bedrocks: Ekaterinovskoe rose granites, megmatites, and nepheline sienites. The largest deposits of the primary kaolins of this region are the Ekaterinovskoe and Bogoroditskoe (Belaya Balka) deposits as well as the Kontsepol'skoe deposit located in Nikolaev Oblast'.

The alkali kaolins of the Ekaterinovskoe deposit, whose development started in 2002, serve as the initial material for obtaining kaolins and feldspars. Alkali kaolins are used to produce high-quality concentrates used in the production of fine ceramic (porcelain-delftware articles) and electrotechnical porcelain as well as construction (ceramic tile and ceramo-granite) and sanitary-ceramic articles. The mineral composition of the kaolin from the Ekaterinovskoe deposit is (%): kaolinite — 26.7; potassium feldspar — 36.1; quartz — 35.1. The sand part comprises, on average, 22.14% of the raw material. The amount of feldspar in sandy part is about 35% [4].

The composition of the kaolins from the Kontsepol'skoe deposit, whose production began at the end of the last century, is the same as that of the kaolins from the Kirovograd and Prosyanovskoe deposits. The latter kaolins are widely used as refractory raw materials as well as raw materials for the ceramic and paper industries.

The chemical composition of kaolin determines its sphere of application. The effect of each component is determined by its amount, the physical composition, and the type of forming mineral. For example, as the content of SiO_2 not bound with Al_2O_3 in clayey minerals increases, the binding power of the clays and their mechanical strength in air-dry and calcined states decreases. The low content of Al_2O_3 content with a high amount of oxides of alkali and alkali-earth metals attests to a low-melting point of kaolin. A large amount of salts of alkali-earth metals (Ca, Mg) appearing in calcites and dolomites increases the porosity, strength, and frost-resistance of ceramic materials and decreases the sintering time and increases shrinkage [8]. The finely dispersed impurities of iron and titanium compounds decrease the brightness of kaolin. At the same time, decreasing the refractoriness of the material and the calcination of the articles, iron impurities are responsible for the formation of dark spots (protuberances and melted material) on the surface of finished products. Titanium compounds give ceramic material a yellow-grey color and intensify the coloration due to the presence of iron. As a result of calcination of the material, predominately in a reducing medium, titanium oxides give a blue – light-blue color. Conventionally, alkali and alkali-earth metals, maintaining a reducing medium during calcination, are introduced in the mix in order to weaken the effect of titanium compounds.

Chemical compositions of natural and enriched alkali kaolins of the main deposits in Ukraine, as determined by specialists from the industry [5 – 7], are summarized in Table 1.

The chemical composition of alkaline kaolins, whose main components are SiO_2 and Al_2O_3, fluctuates over wide limits. This is explained by changes of the content of kaolinite and quartz in rock, which are associated with the particulars of its bedding. For this reason, the characteristics presented are represented by average values. Exceptions are

the data on the kaolin-raw from the Dubrovskoe deposit, which were announced by the producer [4].

In accordance with the operative normative documentation [9] the weight fractions of the main rock-forming oxides should be present in enriched kaolin for production of household and electrotechnical porcelain in the following amounts depending on the brand of kaolin (%): at least 35 – 36 Al_2O_3; no more than 0.6 – 0.9 Fe_2O_3; no more than 0.4 – 0.9 TiO_2; no more than 0.8 – 0.9 CaO. The weight fraction of potassium and sodium oxides is normalized only for KS-1 kaolin, which is intended for the production of sanitary-building ceramic articles. Its value is 3.6%. The ratio of the potassium and sodium oxides (at least 15) is established only for KFP brand kaolin, intended for the production of all forms of ceramic articles. For all other brands of enriched kaolin, irrespective of their spheres of application, these indicators are not normalized.

Thus, on the basis of the main indicators the chemical composition of alkaline kaolins which were presented meets the requirements of the operative normative documentation. An elevated content of alkali and alkali-earth metals confirms that the kaolins from the deposits named belong to the alkali subtype. The high content found for TiO_2 in the enriched kaolin from the Belaya Balka deposit (Donetsk Oblast'), which changes the color of ceramic material in the course of calcination, is compensated by a high content of alkali and alkali-earth metal oxides in the raw material, which lower the chromaticity and which in turn suggests a high brightness and therefore high quality of the finished articles manufacture with adherence to the parameters of the technological process.

It is evident that enriched kaolin contains primarily kaolinite and impurities: quartz, feldspar, and mica as well as the following minerals in the finely dispersed state: zircon, rutile, tourmaline, and pyrite. The amount of SiO_2 after enrichment can be decreased to 50%. Thus, as a result of enrichment of the primary raw kaolin from the Dubrovskoe deposit (see Table 1) the amount of the compounds SiO_2 and TiO_2 decreases and the Al_2O_3 content increases by one-third.

Since alkaline kaolins contain, aside from kaolinite, in different amounts other valuable components — colorless quartz, high-potassium feldspar, fine-flake muscovite, graphite, sillimanite, zircon, rutile, monacite, and minerals, this gives a basis for classifying it as a complex raw material. The presence of feldspar in alkali kaolins suggests that they are similar to porcelain stones.

As a universal raw material, alkali kaolin can be used in the conventional technology for producing porcelain. The high sinterability of porcelain paste obtained with it makes it possible to manufacture articles which are characterized by high mechanical strength, resistance to deformation during calcination, low water-absorption, and complete correspondence of the thermal expansion coefficients of the ceramic material and glaze. The high whiteness of the initial raw material component is a factor that also forms the quite high whiteness of the finished product.

A large part of the kaolins (about 70%) which are mined in Ukraine are subjected to enrichment [10]. The enrichment process is accomplished in three enterprises, which support the development of the three largest deposits of primary kaolins: in Dnepropetrovsk Oblast' — Prosyanovskoe and in Vinnitsa Oblast' — Glukhovetskoe and Turbovskoe. Kaolin from the Prosyanovskoe deposit is recognized as the best of the Ukrainian kaolins.

The enterprises of Ukraine use about 25% enriched kaolin, most of which is exported. The best types of enriched kaolins are used for the production of porcelain and delftware as well as paper and rubber. It has determined that they are suitable for the production of radiotechnical articles, ultramarine, and electrotechnical silumin, and non-wire resistors. Quartz sands washed out during the enrichment of kaolin can be used in the production of glass, fine ceramics, and abrasives. Quartz-feldspar concentrate can find application for the manufacture of glass, the production of rubber-technical articles, and other materials.

Under market economic conditions industry specialists regard the use of complex raw materials as a promising direction in the development of the ceramic and glass industry.

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